Raman spectroscopic study for MgSiO$_3$-perovskite and majorite solid solutions MgSiO$_3$-Mg$_3$Al$_2$Si$_3$O$_{12}$

Hideaki MORISHIMA*, Eiji OHTANI* and Haruo ARASHI**

*Institute of Mineralogy, Petrology, and Economic Geology, Tohoku University, Sendai 980, Japan
**Research Institute for Scientific Measurements, Tohoku University, Sendai 980, Japan

Abstract

Raman spectroscopic studies were made for MgSiO$_3$ perovskite, MgSiO$_3$ garnet, and majorite with compositions of En$_{90}$Py$_{10}$ and En$_{80}$Py$_{20}$ synthesized at high pressure and high temperature. The frequencies of eight Raman active modes of MgSiO$_3$ perovskite were measured at one atmosphere. Three modes with the frequencies, 388, 600 and 937 cm$^{-1}$, were observed for the first time. The frequency of Raman bands of the majorite solid solutions has very weak compositional dependence.

The pressure dependence of the two Raman peaks (602 and 932 cm$^{-1}$ at one atmosphere) of MgSiO$_3$ garnet was measured up to 26.3 GPa using diamond anvil cell; these peaks correspond to the SiO$_4$ internal vibration modes. The Raman frequencies increase linearly with increasing pressure. The mode Grüneisen parameters of these modes are deduced as 0.80 and 0.79.

Introduction

MgSiO$_3$ perovskite is believed to be the most abundant mineral in the lower mantle. Its physical properties have a great influence on the geophysical models of the lower mantle. Thus numerous studies have been made to understand the physical properties of MgSiO$_3$ perovskite. As one of the useful methods to get the lattice dynamical properties of MgSiO$_3$ perovskite, spectroscopic studies have been made (Williams et al. 1987, Wolf and Bukowinski 1987, Hemley et al. 1989). Six Raman active modes of MgSiO$_3$ perovskite have been observed at one atmosphere in the previous works. The frequency of these Raman active modes have been used to put constraints on theoretical models of the lattice dynamics (Williams et al. 1987, Hemley et al. 1989), while it has been expected that MgSiO$_3$ perovskite has 24 Raman active modes from symmetry analysis (Williams et al. 1987). In the present study, we have measured the Raman spectra for MgSiO$_3$ perovskite to find the Raman active modes which were not observed in the previous works.

MgSiO$_3$-rich majorite is one of the most important minerals in the transition zone of the upper mantle, since pyroxene dissolves into majorite with increasing pressure, i.e. the pyroxene-garnet transition (e.g. Kato and Kumazawa 1985). Hence, physical properties such as compressibility, heat capacity, and lattice vibration have been investigated for MgSiO$_3$-rich
majorites (Jeanloz 1981, McMillan et al. 1989, Akaogi et al. 1987, Yagi et al. 1987, Yagi et al. 1992, Yusa et al. 1993). In this paper, we have studied the effects of chemical composition and pressure on the Raman spectra of MgSiO₃-rich majorites.

Experimental

An MA8 multi-anvil high pressure apparatus was used to synthesize the high pressure minerals used for the present Raman measurements. MgSiO₃ perovskite was synthesized by heating for 10 minutes at 1800°C and about 24GPa. MgSiO₃ garnet and majorite with compositions, En₁₀Py₂₀, and En₆₀Py₄₀ were synthesized by heating for 5 to 10 minutes at 1500 to 1800°C and about 17 to 20GPa (where En₁₀Py₂₀ represents the composition of 80mol% MgSiO₃ and 20mol% Mg₃Al₂Si₃O₁₂).

The synthesized crystal quenched from high temperature and high pressure to ambient condition was identified by using the Debye-Scherrer camera with the Gandolfi attachment and the optical microscope. The grain size of synthesized crystals is 10–15 μm.

As the crystal size was small, the micro-Raman system was used to measure the Raman spectrum. The Raman spectra were excited by the 514.5nm line of the Argon-ion laser at the power level of 200mW. The back scattering geometry was used for the present measurements. The laser beam was focused on the surface of the crystal into the spot of 4 μm in diameter by using ×10 objective lens. The Raman spectra of MgSiO₃ garnet was also measured up to 26.3GPa using a lever-type diamond anvil cell. Methanol was used as a pressure transmitting medium. A small chip of ruby was loaded with the sample in order to measure the pressure by using a pressure shift of the ruby fluorescence lines.

Results and discussion

MgSiO₃ perovskite

Figure 1 shows the Raman spectra of MgSiO₃ perovskite at one atmosphere. We observed eight Raman peaks for MgSiO₃ perovskite. The frequencies of peaks observed below 500cm⁻¹, except the peak at 388cm⁻¹, agree well with the previous experiments reported by Williams et al. (1987) and by Hemley et al. (1989) (Table 1). The peaks at 388 and 600cm⁻¹ observed in our experiment were not reported by previous works. These peaks were observed reproducibly in our another measurement. Although periclase and stishovite are possible contaminant phases in the sample, periclase has no Raman active mode and the peaks at 388 and 600cm⁻¹ can not be assigned to stishovite (Hemley et al. 1986). Therefore, these peaks at 388 and 600cm⁻¹ are likely to be the Raman active modes of MgSiO₃ perovskite. Hemley et al. (1989) suggested that there are two peaks at around 370 and 900cm⁻¹ at one atmosphere from extrapolation of their high pressure data. The peak of 937cm⁻¹ observed in our experiment may be identical to their suggested peak of 900cm⁻¹. This discrepancy between our
**Fig. 1.** Raman spectra of MgSiO$_3$ perovskite obtained at one atmosphere.

**Table 1.** Raman peak positions of MgSiO$_3$ perovskite at one atmosphere.

<table>
<thead>
<tr>
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<th>This study</th>
<th>Hemley et al. 1989</th>
<th>Williams et al. 1987</th>
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<td>255 cm$^{-1}$</td>
<td>252 cm$^{-1}$</td>
<td>251 cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>282</td>
<td>283</td>
<td>282</td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>937</td>
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data and the data reported by Hemley *et al.* (1989) may be assigned to the ambiguities due to extrapolation.

*MgSiO$_3$ garnet and majorite solid solution*

Figure 2 shows the Raman spectra of MgSiO$_3$ garnet and majorite solid solutions
(En$_{60}$Py$_{20}$ and En$_{60}$Py$_{40}$). The peaks of MgSiO$_3$ garnet agree well with those reported by McMillan et al. (1989), although some peaks of MgSiO$_3$ garnet reported by them were not observed in our experiment. Two Raman peaks at 573 and 596 cm$^{-1}$ were observed for the majorite with composition En$_{60}$Py$_{20}$ (Fig. 2(a)). On the other hand, it is expected that there is only one strong peak between 560 and 600 cm$^{-1}$ in the spectra for the En$_{60}$Py$_{40}$-majorite, because majorite with another composition have one strong peak between 560 and 600 cm$^{-1}$.
(Fig. 2(b) in this paper, Fig. 3 in McMillan et al. 1989). Thus, one of the two peaks may correspond to impurity in the sample. When the peak position of $\text{En}_{60}\text{Py}_{40}$-majorite (Fig. 2(a)) is compared with that of $\text{En}_{58}\text{Py}_{42}$-majorite reported by McMillan et al. (1989), the peak at 573 cm$^{-1}$ in Fig. 2(a) seems to be a Raman active mode of majorite with $\text{En}_{60}\text{Py}_{40}$ composition.

Figure 3 shows the relationship between chemical compositions and Raman mode frequencies in majorite solid solutions. The peaks corresponding to the SiO$_4$ internal vibration modes and the rotational modes of majorite are shown as the solid lines in Fig. 3; the mode assignment of the Raman peaks was made by comparing the peak positions and intensities of

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**Fig. 3.** Raman frequencies of majorite solid solutions and their compositional dependencies. Solid lines show relationship between chemical composition and Raman mode frequency of majorite corresponding to the SiO$_4$ internal stretching modes ($v_1$, $v_3$), internal bending modes ($v_2$, $v_4$), and the SiO$_4$ rotational mode (R). The relationships are extrapolated to MgSiO$_3$ garnet as the dashed lines. (open circles: McMillan et al. 1989; solid circles: This study).
majorite with those of natural pyrope (Hofmeister and Chopelas 1991). Fig. 3 indicates that the frequencies of the SiO$_4$ vibration and rotational modes are independent of chemical compositions except the 600 cm$^{-1}$ peak ($v_2$). On the basis of IR and Raman spectra of five natural garnets such as pyrope, almandine, spessartine, grossular, and andradite, Hofmeister and Chopelas (1991) have found that the frequencies of SiO$_4$ internal and lattice modes in garnets are affected by the cation mass and size of dodecahedral and/or octahedral sites. It was also found in Fig. 3 that the change in composition, i.e., substitution of Al$_2$ by MgSi in dodecahedral and octahedral sites does not change the mode frequencies of SiO$_4$ internal and rotational modes except the 600 cm$^{-1}$ peak ($v_2$) of which frequency increases with En contents.

The frequencies of SiO$_4$ internal modes of MgSiO$_3$ garnet are considered to be almost equal to those of majorite, because these frequencies are almost independent of chemical composition as discussed above. Hence we think that the peaks at 369, 602, 932, and 1066 cm$^{-1}$ correspond to the SiO$_4$ internal modes.

The pressure dependence of the Raman frequency for the two intense peaks of MgSiO$_3$ garnet (602 and 932 cm$^{-1}$) was measured using a diamond anvil cell up to 26.3 GPa (Fig. 4). The Raman peaks measured at about 15, 20, 26 GPa decreased in intensity and broadened in

![Graph showing pressure dependence of Raman peaks](image)

**Fig. 4.** Pressure dependence of the Raman peaks of MgSiO$_3$ garnet. The value dv/dP for 932 and 602 cm$^{-1}$ peak at one atmosphere is 4.6 and 3.0 cm$^{-1}$/GPa respectively. $\gamma_0$ is calculated by using the relationship, $\gamma_0 = (K_d/c_0) \times (dv/dP)$ with the bulk modulus $K_d = 161$ GPa (Yagi et al. 1992).
TABLE 2. Comparison of the mode Grüneisen parameter of the SiO₄ internal mode among silicate minerals.

<table>
<thead>
<tr>
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<th>γ for SiO₄ internal modes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py - Al</td>
<td>0.6 - 1.1</td>
<td>(Schneider et al. 1990)</td>
</tr>
<tr>
<td>Fo</td>
<td>&lt;0.9</td>
<td>(Chopelas 1990)</td>
</tr>
<tr>
<td>MgSiO₃ garnet</td>
<td>0.8</td>
<td>(This study)</td>
</tr>
</tbody>
</table>

Py: Pyrope
Al: Almandine
Fo: Forsterite

width perhaps owing to solidification of methanol used for the pressure medium. We observed no significant change of the pressure dependency of the Raman frequency due to solidification of methanol. The frequencies of the two modes increase linearly with increasing pressure. The mode Grüneisen parameters were determined as 0.80 and 0.79 for the two modes from the pressure dependence of the Raman frequency obtained in this measurements and the reported bulk modulus of MgSiO₃ garnet, K=161 GPa (Yagi et al. 1992).

The mode Grüneisen parameters determined above probably correspond to those of the SiO₄ internal modes as mentioned above. Table 2 shows that the mode Grüneisen parameters of the SiO₄ internal modes of the other silicate minerals such as forsterite, (see Fig. 3 in Chopelas, 1990) and pyrope (Schneider et al. 1990) together with MgSiO₃ garnet obtained in the present work. Table 2 indicates that mode Grüneisen parameters of the SiO₄ internal modes are similar among various mantle minerals. This implies that the response of the SiO₄ tetrahedron for compression is similar among these mantle minerals.

Conclusions

The frequency of eight Raman active modes of MgSiO₃ perovskite were measured at one atmosphere. We also measured the compositional dependency of the Raman active modes of majorite, En₉₀Py₄₀, En₈₀Py₂₀, and MgSiO₃ garnet. The frequency of SiO₄ internal and lattice modes in majorite solid solution has very weak compositional dependence except the 600 cm⁻¹ peak (ν₂). The value of the mode Grüneisen parameters of the SiO₄ internal vibration modes in MgSiO₃ garnet are about 0.8 which is similar to those of the other mantle minerals.

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References


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